PREPARATION AND CHARACTERIZATION OF EPOXY PARTICLE-FILLED THERMOSETTING COMPOSITES

by

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller
$CaCO_3$	Calcium Carbonate
DGEBA	Diglycidyl Ether of Bisphenol-A
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
FESEM	Field Emission Scanning Electron Microscopy
HCl	Hydrochloric Acid
HEP	Hollow Epoxy Particle
ISO	International Organization for Standardization
MEKP	Methyl Ethyl Ketone Peroxide
SENB	Single Edge Notched Bending
SEP	Solid Epoxy Particle
TGA	Thermogravimetric Analysis

LIST OF SYMBOLS

a	Initial Notch Length
a/W Ratio	Crack Length-to-Width Ratio
b	Specimen Width
b_n	Specimen Width Minus Notch Length
^oC	Degree Celsius
cPs	Centipoise
D	Apparent Diffusion Coefficient
d	Specimen Depth
F	Load Applied
h	Specimen Thickness
K_{IC}	Fracture Toughness
L	Span Length
M_m	Maximum Water Uptake
M_t	Weight Gained at Any Time t
N	Newton
Pa	Pascal
rpm	Revolutions per Minutes
$T_{decomposition}$	Decomposition Temperature
T_g	Glass Transition Temperature
$T_{initial}$	Initial Decomposition Temperature
$tan\ \delta$	Damping Properties
W_d	Sample Dry Weight
W_w	Weight of Sample After Immersed into Water
w	Impact Energy Absorbed
$wt\ \%$	Percentage by Weight
y	Geometrical Correction Factor
σ_f	Flexural Strength

PENYEDIAAN DAN PENCIRIAN KOMPOSIT TERMOSET TERISI PARTIKEL EPOKSI

ABSTRAK

Teknik emulsi berasaskan air telah digunakan dalam kajian ini untuk menghasilkan partikel epoksi berongga (HEP) dan partikel epoksi pejal (SEP). Pengisi HEP dan SEP dirawat secara kimia dengan menggunakan larutan asid hidroklorik untuk menyingkirkan kalsium karbonat yang berlebihan di atas permukaan pengisi. Kajian ini mendapati bahawa pengisi HEP dan SEP boleh dihasilkan secara optimum pada masa homogen selama 9 minit dan 7 minit di bawah kelajuan homogen 15,000 rpm, masing-masing. Pengisi HEP ditambahkan ke dalam matrik epoksi, ester vinil dan poliester pada jumlah kandungan yang berlainan (0-9 wt%) untuk menguatkan dan meliatkan matrik termoset. Sifat-sifat mekanik optimum (i.e., keliatan rekahan, kekuatan hentaman, kekuatan tensil, modulus tensil dan kekuatan lenturan) bagi komposit terisi HEP dapat dicapai dengan penambahan 3, 5 dan 5 wt% kandungan pengisi HEP ke dalam matrik epoksi, ester vinil dan poliester masing-masing. Penguatan dan perliatan ke atas komposit terisi HEP melibatkan pengikatan matrik termoset ke dalam kawasan berongga pada pengisi HEP. Walau bagaimanapun, penambahan kandungan pengisi HEP berlebihan di dalam matrik termoset membawa kepada kemerosotan sifat-sifat mekanik komposit. Hal ini disebabkan oleh penggumpalan antara pengisi-pengisi HEP yang mewujudkan kawasan penumpuan tegasan. Kajian ini juga mendapati bahawa penambahan pengisi HEP ke dalam matrik termoset telah meningkatkan suhu peralihan kaca, kestabilan terma, dan modulus storan komposit. Penyerapan air dan pekali peresapan komposit juga meningkat dengan peningkatan kandungan pengisi HEP daripada 0 hingga 9 wt%.

PREPARATION AND CHARACTERIZATION OF EPOXY PARTICLE-FILLED THERMOSETTING COMPOSITES

ABSTRACT

Water-based emulsion technique was used in this study to produce hollow epoxy particles (HEP) and solid epoxy particles (SEP). The HEP and SEP fillers were then chemically treated with hydrochloric acid solution to get rid of the excessive calcium carbonate on the surfaces of the fillers. It was found that HEP and SEP fillers could be optimally prepared at the homogenizing time of 9 minutes and 7 minutes, respectively under the homogenizing speed of 15,000 rpm. HEP fillers were added into the epoxy, vinyl ester and polyester thermosetting matrices at different loading amounts (0-9 wt%) to strengthen and toughen the thermosetting matrices. The optimum mechanical properties (i.e., fracture toughness, impact strength, tensile strength, tensile modulus and flexural strength) of the HEP-filled composites could be achieved by the addition of 3, 5 and 5 wt% of the HEP filler content into the epoxy, vinyl ester and polyester matrix, respectively. The strengthening and toughening of the HEP-filled composites involved the interlocking of thermosetting matrices into the pores regions of the HEP fillers. However, the addition of excessive HEP loading into the thermosetting matrices led to the deterioration of the mechanical properties of the composites. This was attributed to the agglomeration of the HEP fillers among themselves, creating stress concentration area. It was also found that the addition of HEP fillers into the thermosetting matrices increased the glass transition temperature, thermal stability, and storage modulus of the composites. The water absorption and diffusion coefficient of the composites also increased with increasing the HEP loading, varying from 0 to 9 wt%.

CHAPTER 1

INTRODUCTION

1.1 An Introduction to Filler Microspheres

Filler is a substance added into the polymer matrices to tailor and improve the properties of the polymer as well as to lower the production cost of a polymer (Alger, 1997). Due to the fact that fillers could bring along numerous advantages, plenty of fillers have been widely explored and introduced into the polymer matrices. In recent years, filler microspheres (i.e., solid filler microspheres & hollow filler microspheres) have attracted the interest of researchers worldwide and have been widely developed to replace the mineral fillers (Dufton, 1998). The development of filler microspheres is mainly attributed to the spherical structure, non-cohesive and hydrolytically stable of the microspheres (Klempner et al., 2004). In contrast to that of conventional fillers (i.e., mica, calcium carbonate, silica, etc) which possess irregular structure and shape, filler microspheres is more advantageous in terms of their spherical structure (Lubin & Peters, 1998; Katz & Milewski, 1987). This is because the isotropic nature of the filler microspheres give rise to uniform and homogeneous distribution of applied forces throughout the polymer matrices. Furthermore, Stuart (1992) also stated that the addition of filler microspheres into the polymeric matrices is not influence the viscosity of the compound.

Nowadays, a variety of processing methods have been developed to fabricate different types of filler microspheres. Particularly, Cheng et al. (2005) stated that solid ceramic microspheres can be prepared using wet-chemical method, high temperature melting method and spray drying method. Stuart (1992) used the softening process on irregular glass particles to produce solid spherical glass

microspheres. Yang et al. (2010) manufactured the hollow carbon microspheres through a one-step oxidation-in-air process. Toshiharu (1999) found that hollow calcium carbonate microspheres can be fabricated using the interfacial reaction method. Singh et al. (2007) mentioned that hollow silica microspheres can be synthesized through the sol-gel and emulsion methods. In addition, Du et al. (2011) developed porous epoxy microspheres with a number of holes on their surfaces via the advanced aqueous emulsion method.

1.2 Emulsion Method

Traditionally, emulsion method is commonly used in many industries, such as food, pharmaceutical, paint, printing, etc (Binks, 1998; Xu et al., 2011). Nowadays, emulsion method is utilized to produce hollow microspheres. This is attributed to the fact that emulsion method is an easy, economical and controllable method to produce hollow microspheres with desirable shape and surface properties (Singh et al., 2007). Basically, emulsion is a thermodynamically unstable system consisting of one liquid dispersed in another insoluble liquid. The emulsion process commonly requires the use of surfactant and energy inputs provided by the homogenizers, ultrasonicators or high-speed blenders (Calderon et al., 2007; Perrechil & Cunha, 2010; Sakai, 2008). Creaming, flocculation, coalescence and Ostwald ripening are the typical mechanism that takes place during emulsion destabilization (Rousseau, 2000; Binks, 1998).

According to Kamarudin et al. (2010), it was determined that homogenizing speed and homogenizing time are two major factors influencing the droplets' size in the emulsion system. Specifically, the particle size of the droplets reduces when subjected to a higher homogenizing speed and homogenizing time. This phenomenon is attributed to the increase in shear force if the homogenizing process is performed

for a longer period of time and at a higher speed (Yong et al., 2004). Zhao et al. (2007) also mentioned that higher shear force reduces the emulsion viscosity and subsequently decreases the size of the droplets.

1.3 Attraction of Hollow Sphere Particles

Thermosetting materials have been widely utilized in a variety of industrial applications. This is attributed to their good chemical resistance, superior mechanical and thermal properties as well as their ease of processing (Wetzel et al., 2006; Park et al., 2005). However, the brittleness of most thermosetting materials has limited most of their uses and applications which require good toughness properties (Astruc et al., 2009). Therefore, plenty of efforts have been implemented to get rid of the brittleness of the thermosetting materials. The commonly used methods are the incorporation of elastomers into the thermosetting matrices (Thomas et al., 2008); and the use of rigid inorganic fillers (i.e., calcium carbonate, clays, talc, or kaolin) to enhance the toughness of thermoset (Astruc et al., 2009). In recent years, an alternative method to improve the modulus, hardness and toughness of thermosetting materials is the utilization of hollow sphere particles. For example, Du et al. (2011) and Liew (2009) added the porous epoxy microspheres into the thermosetting matrices to reinforce the thermosets.

Apart from showing their potential applications to reinforce and toughen the polymeric materials, hollow sphere particles are also used as fillers to improve the water absorption properties of membranes, and to modify the dielectric properties of epoxy (Watanabe et al., 2009; Chen et al., 2010; Yuan et al., 2008; Yung et al., 2009). According to Watanabe et al. (2009) and Liang & Li (2007), the extensive use of hollow sphere particles in a variety of industrial applications is attributed to the unique properties of hollow particles such as low density, low thermal conductivity

coefficient, surface permeability, and large surface area. Moreover, hollow sphere particles are also advantageous over other conventional fillers due to their spherical structure (Katz & Milewski, 1987). Accordingly, the undesirable stress concentration areas between the polymer-filler interfaces could be avoided as a result of the smooth spherical surfaces of the hollow particles (Liang & Li, 2007).

1.4 Problem Statement

A lot of techniques have been developed and implemented by researchers to produce both solid and hollow filler microspheres nowadays. However, each technique has its own problems. This is owing to the fact that some of these techniques need sophisticated equipments and high processing temperature as well as pressure to produce filler microspheres. Also, the filler microspheres produced using the conventional methods (i.e., interfacial reaction method, one-step oxidation-in-air process, template-based solvent evaporation method, etc) commonly possess closed cell structure and have no and/or few holes on their surfaces.

The brittleness of thermosetting material is the main factor limiting their end-used applications. A variety of fillers have been added into the thermosetting matrices to enhance their toughness. However, the addition of large amount of fillers into the thermosetting matrices gives rise to an increase in production cost and a reduction in pot life during processing. Also, the addition of fillers that possess irregular shape and structure tend to increase the stress concentration areas in the thermosetting matrices and eventually reduces the properties of the composites.

1.5 Hypothesis and Motivation

It is hypothesized that hollow epoxy particles (HEP) and solid epoxy particles (SEP) fillers can be prepared by using the water-based emulsion technique, which is

simple and more environmental friendly. Also, the HEP fillers with plenty number of holes on their surfaces and the SEP fillers with a smaller particle size is prepared under the optimum homogenizing speed and homogenizing time. The excessive calcium carbonate present on the surface of HEP and SEP fillers can be removed by using the hydrochloric acid treatment. It is also believed that the processing parameters (i.e., homogenizing speed and homogenizing time) affect the morphology, particle size and the number of holes present on the surface of HEP and SEP fillers. The amount of HEP filler content added into thermosetting matrices influences the mechanical, thermal and physical properties as well as the water uptake of the HEP-filled composites. Also, it is believed that the thermosetting matrices interlock into the pore regions of the HEP fillers.

1.6 Research Objectives

The objectives of this present study are:

1. To produce HEP filler using polyamide and SEP filler using polyamine and to investigate the effect of processing parameters (i.e., homogenizing speed and homogenizing time) on the formation, size, structure morphology and shape of HEP and SEP fillers prepared using emulsion technique.
2. To characterize the effect of hydrochloric acid (HCl) treatment on the surface morphology and physical properties (i.e., particle size, surface area, density, pore size and pore diameter) of HEP and SEP fillers produced.
3. To study the effect of HEP filler loading on the physical, mechanical, thermal properties and water absorption behaviour of HEP-filled epoxy, vinyl ester and polyester composites.

CHAPTER 2

LITERATURE REVIEW

2.1 Classification of Fillers

Fillers are finely divided solid materials incorporated into the polymer matrix to improve the commercial uses of polymer and to reduce the cost of the polymer. Generally, the addition of fillers make the polymer compound stiffer and harder compared to that of the pure compound (Alger, 1997). However, these fillers are not alter the molecular structures of the polymer (Brydson, 1999; Rothon, 2001; Shenoy, 1999). There are plenty of different types of fillers around the world. The wide range of fillers are commonly categorized according to their shapes, forms, sizes, chemical structures as well as their inherent properties (Xanthos, 2010). Table 2.1 displays the classification of fillers according to their shapes and physical forms.

Table 2.1: Classification of filler based on their physical forms (Shenoy, 1999)

Physical Form	**Shape**	**Example of Filler**
One-Dimensional	Whiskers Fibers	Wollastonite Glass Fibers
Two Dimensional	Platelets Flakes	Clay Mica
Three-Dimensional	Ellipsoidal Spherical	Wood Flour Glass Beads

Table 2.2 shows the classification of fillers based in their chemical structures. Accordingly, fillers can be subdivided into two main groups (i.e., organic fillers and the inorganic fillers). Cellulosic, proteins, lignin and synthesis polymers are several examples of the organic fillers. Carbonates, oxides, silicate, sulfate and metal powder are several typical examples of inorganic fillers.

Table 2.2: Classification of filler based on their chemical families (Xanthos, 2010)

Chemical Families		Example of Fillers
Organic Fillers	Natural polymers	Cellulose fibers, wood flour and fibers, flax, cotton, sisal and starch
	Carbon, graphite	Carbon fibers, graphite fibers and flakes, carbon black and carbon nanotubes
	Synthesis polymers	Polyamide, polyester aramid and polyvinyl alcohol fibers
Inorganic Fillers	Oxides	Glass (fibers, spheres, hollow spheres and flakes), MgO, SiO_2, Sb_2O_3, Al_2O_3 and ZnO
	Salts	$CaCO_3$, $BaSO_4$, $CaSO_4$, phosphates and hydrotalcite
	Hydroxides	$Al(OH)_3$ and $Mg(OH)_2$
	Silicates	Talc, mica, kaolin, feldspar, wollastonite montmorillonite, and asbestos
	Metals	Boron and steel

Table 2.3 shows the classification of fillers based on their inherent properties. Fillers are able to be distinguished by their inherent properties since each of specific fillers possesses its own specific function. For example, some filler play the role to reinforce and subsequently modify the end properties and performance of the final product whereas, some are able to tailor the processing characteristics or even reduces the cost of production (Alger, 1997; Lubin & Peters, 1998; Xanthos, 2010).

Even if there are various fillers available worldwide nowadays, the selection of appropriate fillers for certain applications should be seriously taken into account. The wrong selection of fillers not only deteriorates the properties of the compounds, but also leads to an increment in the overall production costs. In general, selection of fillers highly depends on the costs and availability. Apart from that, the compatibility of the fillers with the matrix, thermal stability, toxicity and recyclability should also take into considerations (Klyosov, 2007; Shenoy, 1999). Last but certainly not least, the filler content and the processability of the filler-filled compounds are also factors which should be considered before choosing any type of fillers.

Table 2.3: Classification of filler based on their specific functions (Shenoy, 1999; Xanthos, 2010)

Function	Example of Fillers
Cost savings	Wood flour, saw dust, cotton flock
Reinforcement	Glass fibers, cellulosic fibers, synthetic fibers, asbestos fibers
Hardness	Metallic powders, mineral powders, silica, graphite
Thermal insulation	Asbestos, ceramic oxides, silica
Chemical resistance	Glass fibers, synthetic fibers, metallic oxides, graphite
Degradability	Organic fillers, starch and cellulosic fibers
Enhancement of processability	Thixotropic, antisag, colloidal silica, acid scavengers and hydrotalcite
Modification of surface properties	Antiblock, lubricating: silica, $CaCO_3$, PTFE, MoS_2 and graphite
Improved dimensional stability (Isotropic shrinkage and reduce warpage)	Particular fillers, glass beads and mica
Control of damping	Flake fillers, glass and $BaSO_4$

2.2 Filler Microspheres

In recent years, filler microspheres have been widely fabricated by plenty of researchers around the world from ceramic, glass, polymer, carbon and metal (Ye et al., 2004). This growing trend is mainly attributed to the unique properties exhibited by the filler microsphere such as strong, isotropic, non-cohesive, moisture resistance, and hydrolytically stable compared to that of the conventional fillers (Klempner et al., 2004). Furthermore, Lubin & Peters (1998) also mentioned that the spherical structure of filler microspheres is more advantages than the conventional fillers, such as mica, calcium carbonate, silica and talc, which possess irregular shape. This is owing to the fact that the isotropic nature of the filler microspheres makes them able to distribute the forces applied throughout the polymeric matrix uniformly and homogeneously. In addition, the addition of filler microspheres with smaller surface area to volume ratio into the matrix is not significant increases the viscosity of the compound (Katz & Milewski, 1987; Stuart, 1992). This permits the addition of a

higher loading of fillers into the matrix and subsequently reduces the overall production cost of the final product. Klempner et al. (2004) also agreed that the viscosity of the filler microspheres-filled system is lower than that of the system filled with irregular-shape fillers.

Accordingly, filler microspheres can be further divided into two main groups (i.e., solid filler microspheres and hollow filler microspheres). Stuart (1992) reported that the solid microsphere fillers are commonly made up of glass, ceramics, graphite, carbon and/or plastics like acrylic and styrene. Arthur (1995) reported that the hollow microsphere fillers can be produced from epoxy resin, rubber, glass, silicone, carbon, ceramic and/or polymers like phenolic and polyvinylidene chloride.

2.2.1 Solid Filler Microspheres

2.2.1.1 Glass Microspheres

Solid glass microspheres commercially appear in the forms of white powders. They are commonly used as reinforcing fillers, especially in the plastic industry. This is mainly attributed to the unique properties of solid glass microspheres, such as low cost and good chemical inertness (Stuart, 1992). In addition, Wilkes et al. (2005) also determined that the addition of solid glass microspheres into the injection-molded poly (vinyl chloride) formulation helps to tailor and improve the dimensional stability of the final product. The particle size of the solid glass microspheres is found to be in the range of 10-150 μm, and the density is about 200-400 kg/m^3 (Klempner et al., 2004). According to Stuart (1992), the solid glass microspheres can be manufactured once the irregular particles of glass are subjected to the softening process. The surface tension of the natural shape causes them to flow into the spherical shape, and lead to the production of solid glass microspheres.

2.2.1.2 Ceramic Microspheres

Ceramic microspheres are unique, semi-transparent fine particles engineered to reduce costs, enhance properties and to improve the processability. Generally, the ceramic microspheres are added into the polymers to prevent the plasticity reduction in the composite materials. This is owing to the fact that the addition of solid ceramic microspheres could get rid of the stress concentration area at the edges of anisotropic reinforcing like the fillers with irregular geometries (Cheng et al., 2005). In addition, Suryavanshi & Swamy (2002) also reported that the solid ceramic microspheres offer the advantages of low bulk density and the enhancement in the thermal, mechanical and chemical properties of the ceramic microspheres-filled compounds. Traditionally, ceramic microspheres are formed naturally from coal burning coalesce (Stuart, 1992). These ceramic microspheres can also be produced using wet-chemical method, high temperature melting method and spray drying method (Cheng et al., 2005).

2.2.1.3 Plastic Microspheres

Plastic microspheres are commonly manufactured through the polymerization process when the aqueous suspension is heated and agitated (Stuart, 1992). The plastic microspheres can be prepared from thermoplastic and thermosetting materials. Epoxy microspheres, polyethylene microspheres, and polystyrene microspheres are three typical examples of solid plastic microspheres. Solid epoxy microspheres could be utilized as the reinforcing fillers (Ng, 2009), whereas thermoplastic microspheres especially the solid polyethylene microspheres commonly premix with pigments and additives to produce colourful microspheres (Lipovetskaya, 2011). The microspheres could be produced in a wide range of colours. The addition of coloured microspheres makes them to be visualized easily on the surface of a material or in a solution.

2.2.2 Hollow Filler Microspheres

Hollow microspheres have attracted the interest of most researchers in recent years (Huang et al., 2009; Chen et al., 2010). This is due to the fact of those hollow microspheres not only show their potential applications as filler to reinforce materials, but also serve the purpose in drug delivery, controlled release, membrane application, absorptive filters as well as confined reaction vessel (Watanabe et al., 2009; Hwang et al., 2009; Ding et al., 2006). Furthermore, the unique properties of the hollow microspheres such as low density, low thermal conductivity coefficient, and surface permeability make these hollow microspheres appropriate to be utilized in various applications (Watanabe et al., 2009; Liang & Li, 2007). In addition, Zhao et al. (2008) and Huang et al. (2009) stated that hollow microspheres are appropriate to be used as low weight fillers for most materials since their specific structures have the ability to accommodate relatively large objects and give rise to the "micro-package" effect. Apart from that, Liang & Li (2007) also proved that the smooth spherical surfaces of hollow microspheres do not generate undesirable stress concentration area between the polymer-filler interface.

Considering these advantages as mentioned, much efforts have been made to synthesize, develop and utilize the hollow microspheres in various filler applications. For example, hollow calcium carbonate has been utilized as paper filler; hollow glass microspheres are used as fillers to improve and modify the dielectric properties of the epoxy thermoset and the hollow mesoporous silica microspheres are used to improve the water absorption properties and photon conductivity of the membranes (Chen et al., 2010; Watanabe et al., 2009; Yuan et al., 2008; Yung et al., 2009). Liang & Li (2007) also reported that hollow ceramic beads and the rigid hollow plastic beads can be used as the building materials, space light and in the aviation industry.

2.2.2.1 Hollow Silica Microspheres

Hollow silica microspheres can be typically fabricated using a lot of methods, such as soft template, hard template, colloidal template by layer-by-layer method, sol gel or emulsion method, spray drying method, coaxial-nozzle method as well as the microfluidic technique (Chen et al., 2010; Zhang et al., 2003; Li et al., 2010; Singh et al., 2007). Moreover, Hwang et al. (2009) reported that the hollow silica microspheres can be prepared using the amine functional polymeric microsphere as template. Accordingly, the polymeric microspheres are produced once the 2-dimethylaminoethyl methacylate and methylmethacrylate dispersed in supercritical carbon dioxide are copolymerized. Specifically, the silica oligomers show the tendency to condense on the surface of the polymeric particles under the hygrothermal process in water, tetreethylorthosilicate and ethanol mixtures due to the different charges. This subsequently results in the formation of a core-shell polymeric particle. The hollow silica microspheres with a cavity hole at their centres are produced when the core of the polymer particles are removed during the calcination process. Figure 2.1 illustrates the formation of the hollow silica microspheres using the amine functional polymeric microspheres as the template.

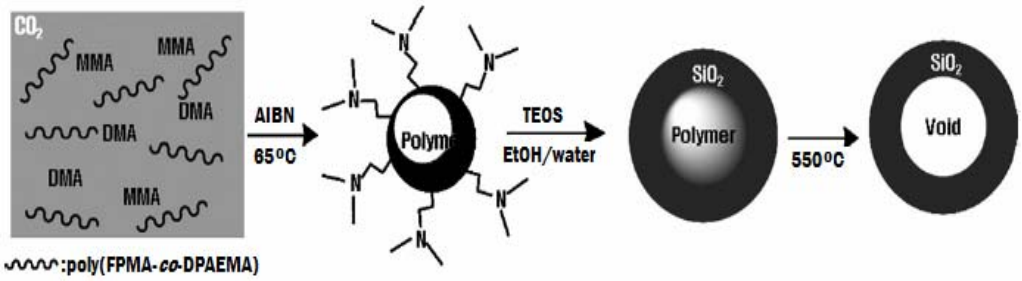

Figure 2.1: Schematic illustration of the formation of hollow silica microspheres (Hwang et al., 2009)

2.2.2.2 Hollow Glass Microspheres

Hollow glass microspheres are commonly used as light-weight fillers in the polymer system and as fillers to produce acoustic and thermal materials (Zhang et al., 2005; Budov, 1994; Xu et al., 2007; Wilkes et al., 2005; Liu et al., 2007). Yung et al. (2009) also stated that hollow glass microspheres are commonly introduced into the epoxy resins to improve the dielectric properties of the composite materials. Hollow glass microspheres are widely used in various applications since their outer stiff glass and inner inert gas have offered various unique properties, such as light weight, high thermal and acoustic insulating, low dielectric constant and high wear resistance (Xu et al., 2007; Budov, 1994; Yung et al., 2009; Zhang et al., 2005). However, their low crush strength makes them impossible to be used in high pressure injection moulding and extrusion moulding process (Wilkes et al., 2005).

Figure 2.2 displays the preparation process of the hollow glass microspheres. Initially, the glass frits which are heated over their glass transition temperatures become softer, and the gaseous is released from the blowing agent. This result a surface tension on the glass melts. This phenomenon eventually leads to the formation of a cavity hole at the centre of the sphere particles. These particles would then be forced out from the flame and subjected to a fast cooling process. As a result, the hollow glass microspheres are produced (Geleil et al., 2006). The hollow glass microspheres are formed once the irregular frits are being heated, followed by rapid cooling when they are forced out from the gas flame (Stuart, 1992). In addition, Stuart (1992) also reported that the addition of blowing agent, especially the sulphur, is significantly influence the production of hollow glass microspheres.

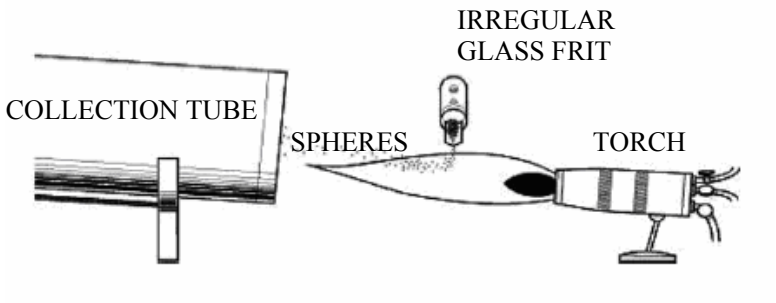

Figure 2.2: Production process of hollow glass microsphere
(Geleil et al., 2006)

2.2.2.3 Hollow Calcium Carbonate Microspheres

Hollow calcium carbonate microspheres have been utilized as fillers for the recycled papers (Toshiharu, 1999). Recently, hollow calcium carbonate microspheres are also used in various industrial applications, such as fillers for plastics and rubber, drug delivery, agrochemical, pharmaceuticals and paint (Hadiko et al., 2005; Tang et al., 2007). This is mainly due to the low weight and high specific light scattering of the hollow calcium carbonate microspheres (Watanabe et al., 2009).

A variety of fabrication techniques have been utilized to prepare the hollow calcium carbonate microspheres. Cai et al. (2008) reported that organic template and carbon dioxide-bubbles template are two typical methods used to produce the hollow calcium carbonate microspheres. However, these methods give rise to low yield and non-uniform morphology of the hollow calcium carbonate microsphere. In order to overcome these limitations, Toshiharu (1999) suggested the use of an effective and simple interfacial reaction method to prepare the hollow microspheres. As shown in Figure 2.3, the potassium carbonate solution is pre-mixed with the benzene solution dissolved in a polyoxyethylene sorbitan monoolate surfactant. The mixture was then subjected to the emulsion process by using the ultrasonic irradiation, followed by the homogenization process. Then, the emulsified mixture is stirred homogeneously with the calcium chloride solution consisting of a high concentration of calcium ions. The

calcium ion chemically reacts with the carbonate ions to generate vaterite. The vaterite is then change into calcite and substitute the oil membrane of the droplets. The hollow calcium carbonate microspheres are formed once the mixture is being subjected to the filtering and drying processes.

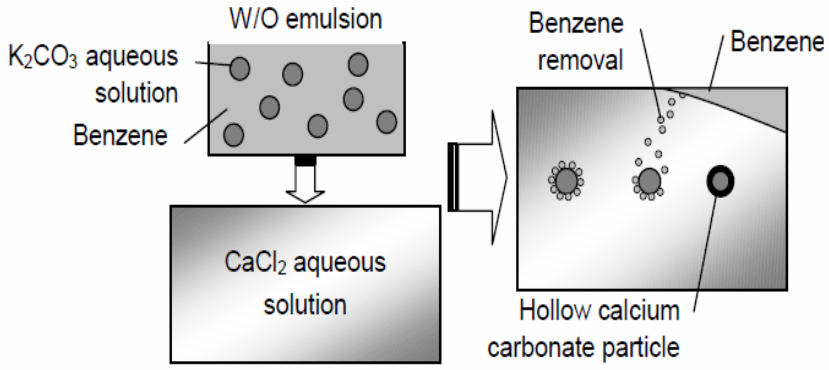

Figure 2.3: Schematic illustration of the formation of the hollow calcium carbonate microspheres by the interfacial reaction method (Toshiharu, 1999)

2.2.2.4 Hollow Polymer Microspheres

Template-based solvent evaporation technique is commonly used to fabricate the micro-scale and nano-scale hollow polymer microspheres. Figure 2.4 displays the production of hollow polymer microspheres by using the method of template-based solvent evaporation. Generally, poly (lactic-*co*-glycolic acid) (PLGA) playing the role as the sacrificial core of hollow particles was added into the polymer-water solutions. The surface of the PLGA particles are then be coated with a layer of polymer during the acetone evaporation reaction. Then, ammonium persulfate solution and ascorbic acid were added into the mixture to induce the crosslinking process and to make the outer layer of polymer stronger. Hollow polymer particles are obtained once the PLGA core was dissolved into the tetrahydrofuran solution (Cao et al., 2011).

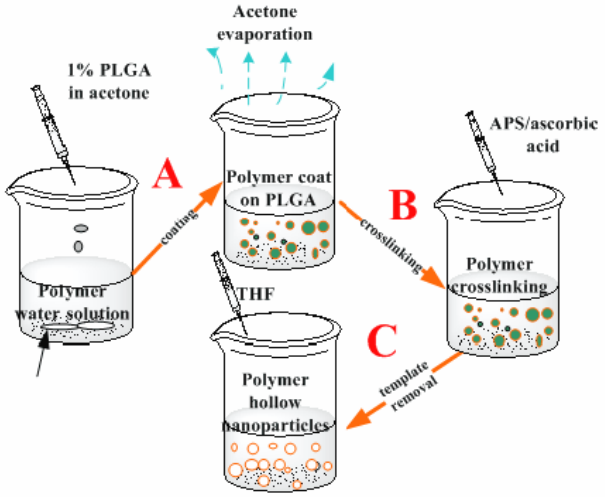

Figure 2.4: The fabrication method of hollow polymer nanoparticles
(Cao et al., 2011)

Du et al. (2011) also reported that the porous epoxy microparticles with cavity holes around their surfaces can be produced by using the emulsion technique recently. Accordingly, the porous epoxy microspheres can be generated by allowing the epoxy droplets maintaining in the form of partial coalescence in the oil-in-water solutions before being thermally cured and grinded into powders. Calcium carbonate acting as dispersing agent during the emulsion process plays an important role in the formation of porous epoxy microspheres. This is due to the fact that the calcium carbonate prevents and slows down the coalescence between the epoxy droplets and subsequently gives rise to the formation of cavity holes on the surfaces once the calcium carbonates precipitate out from the epoxy droplets under high homogenizing speed.

2.2.2.5 Hollow Carbon Microspheres

Various methods have been used to fabricate the hollow carbon microspheres. For example, Lai et al. (2010) reported the hard template method to manufacture the

hollow carbon microspheres. Yang et al. (2010) suggested a one-step oxidation-in-air process as displayed in Figure 2.5 to produce the hollow carbon microsphere without the need of any chemical reagents. As an overall view for this one-step oxidation-in-air process, the solid carbon microspheres are heated in air at 450-550^{o}C. The outer diameter of the solid carbon microspheres is then reduced gradually during the oxidation process and the carbon dioxide gas is released. This results in the formation of the hollow carbon microspheres after a particular time frame. However, it was found that the hollow carbon microspheres are broken down and burned if the oxidation process is too long.

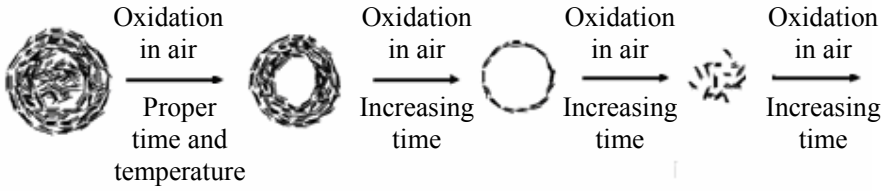

Figure 2.5: Schematic represented the one-step oxidation-in-air process of hollow carbon microspheres (Yang et al., 2010)

2.3 Emulsion

Emulsion is described as a heterogeneous system consisting of a liquid phase dispersed into another liquid phase in the presence of a surface active agent (Singh et al., 2007; Mason, 1999; Graaf et al., 2005; Calderon et al., 2007; Perrechil & Cunha, 2010; Pal, 2011). The emulsion process commonly involves the energy input, such as the high speed blenders, ultrasonicators, rotor-stator system, and/or homogenizers, to generate a strong shearing stress to disperse one fluid into another immiscible liquid (Perrechil & Cunha, 2010). Surface active agents such as the amphiphilic polymers or the surfactant are added to reduce the interfacial tension between the two different phases, and to make the emulsion process easier (Pal, 2011; Sakai, 2008).

Generally, emulsion can be classified into two main categories (i.e., water-in-oil and oil-in-water) (Singh et al., 2007). The oil-in-water emulsion is a process or a system in which oil droplets are dispersed throughout the continuum of water phase, whereas water-in-oil emulsion is a system made up of the water droplets dispersed in the continuum of immiscible oil phase (Pal, 2011). These emulsion process could be used in food, cosmetic, paint, pharmaceutical, agrochemical and oil industries (Sakai, 2008). Recently, oil-in-water emulsion process is also used to produce porous epoxy microspheres (Du et al., 2011).

Emulsion process is typically thermo-dynamically unstable. This is attributed to the relatively high interfacial tension between the water phase and oil phase (Goff, 1997; Singh et al., 2007; Graaf et al., 2005; Perrechil & Cunha, 2010). According to Rousseau (2000), the emulsion destabilization is highly influenced by the processing conditions, compositions and environmental conditions. Basically, the destabilization process of emulsion comprises four mechanisms, such as creaming, flocculation, coalescence and Ostwald ripening as shown in Figure 2.6 (Tcholakova et al., 2006). In general, the creaming and flocculation process are precursors for the coalescence, whereas the Ostwald ripening is the last stage of the emulsion process (Mohos, 2010). Tcholakova et al. (2006) reported that Ostward ripening tends to take place once the distribution of droplet size changes with the processing time. Burgess & Yoon (1995) mentioned that coalescence and Ostwald ripening are two main factors influencing the growth of the droplet size.

Creaming refers to an undesirable and inevitable process during the emulsion. This process commonly occurs during storage mainly because of the destabilization of the system (Perrechil & Cunha, 2010). The difference in mass density between the dispersed oil and the continuous water phase lead to the phase separation (Edwards,

2007). Droplets with lower density move upwards and cream, whereas droplets with higher density tend to move downwards and sediment at the bottom (Kasapis et al., 2009; Mohos, 2010). Perrechil & Cunha (2010) stated that the resistance against that creaming can be increased by minimizing the density difference between the oil phase and water phase, as well as reducing the size of the droplets.

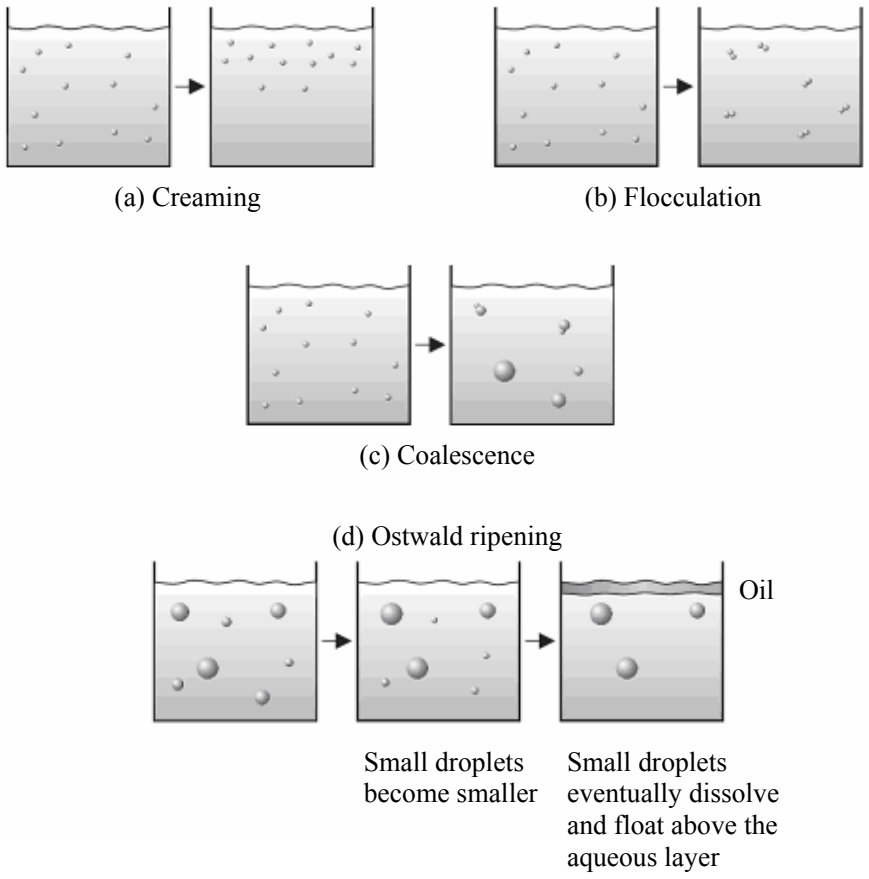

Figure 2.6: Common mechanisms in the emulsion destabilization: (a) creaming, (b) flocculation, (c) coalescence and (d) Ostwald ripening (Tamime, 2007)

According to Kasapis et al. (2009), the collided emulsion droplets show their ability to aggregate among each other forming a larger clump during the flocculation stage. However, reversible aggregation tends to take place due to the weak attractive force between the emulsion droplets. Myers (2006) also reported that these emulsion

droplets are unable to combine and merge into a single unit even though aggregation of the emulsion droplets tends to form during flocculation. This eventually causes the clump to be re-dispersed by the agitation forces applied (William & Phillips, 2008; Dukhin et al., 2001). According to Mohos (2010) and Goff (1997), a bigger and larger emulsion droplet would only be formed once the emulsion droplets with smaller size collide against each other during the coalescence stage. This phenomenon takes place since these emulsion droplets which are thermo-dynamically unstable tend to achieve emulsion stabilization during coalescences. This eventually leads to an increment in the droplet's size and a reduction in the interfacial area of the droplets between the aqueous and oil phases. According to Tamime (2009), the coalescences rate of these droplets can be accelerated under high shear stress. This is due the fact that there is a driving force to reduce the surface free energy and a decrease in the viscosity of the dispersed phase. The strong attraction forces between the dispersed droplets and the low resistance of the droplets against rupture give rise to coalescence (Mitidieri & Wagner, 2002).

Commonly, low-molar-mass surfactant and hydrocolloids are added into the emulsion to form a barrier between the continuous phase and the dispersed phase, as well as to raise the viscosity of the outer phase, in order to prevent the droplet from coalescence (Sovilj et al., 2004). This is due to the fact that the surfactant reduces the interfacial tension between the oil phase and water phase, and eventually stabilizes the newly formed droplets (Kamarudin et al., 2010). Apart from that, increase in the viscosity of the continuous phase would restrict the mobility of the droplets and then lead to the reduction of the collision frequency. The drainage time is extended longer while the collision time is remaining the same. Thus, longer drainage time than collision time would reduce the coalescence possibility of the droplets. Tesch &

Schubert (2002) also mentioned that higher viscosity of the continuous phase would give rise to lower coalescence possibility. According to Equation 2.1, the coalescence possibility of droplets can be determined according to the ratio of the drainage time and the collision time (Dickinson & Miller, 2001).

$$P = \exp\left(- \frac{t_{drain}}{t_{coll}} \right) \tag{2.1}$$

where P = Coalescence possibility, t_{drain} = drainage time, and t_{coll} = collision time

In addition, it is also noted that the coalescence becomes incomplete if crystals are present in the oil phase. This is due to the fact that these crystals tend to hinder the droplets from merging among each other during the coalescence process. Incomplete coalescence is one of the mechanisms giving rise to the emulsion instability (Rousseau, 2000). According to Fredrick et al. (2010), the crystals present in the oil phase tend to stick together and aggregate among each other by the Van der Waals force. This eventually induces the formation of crystal networks within the emulsion droplets and lead to the incomplete coalescence of the dispersed droplets. However, a few crystals surrounding the outer surface of the dispersed droplets still penetrate through the intervening layer, and subsequently protrude into another dispersed droplet as shown in Figure 2.7. As a result, both droplets tend fuse together and form into a single unit by the oil-oil contact. This lowers the surface area of the particle to be exposed in the aqueous phase (Kasapis et al., 2009).

Also, Vanapalli & Coupland (2001) reported that the distance in between the emulsion droplets should not be greater than that of the size of the crystal protruded. This could benefit the crystal to pierce successfully through the intervening layer of the droplet during the partial coalescence process. Moreover, Fredrick et al. (2010)

stated that the velocity gradient is also one of the important factors in altering the rate of the partial coalescence process in the emulsion destabilization system.

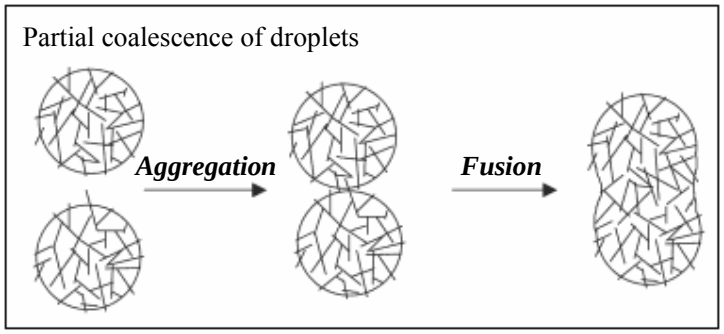

Figure 2.7: Schematic illustrated the mechanism of partial coalescence (Kasapis et al., 2009)

2.4 Thermosetting Materials

2.4.1 Epoxy Resin

Epoxy resins are one of the thermosetting materials containing two or more epoxy functional groups in their polymer backbone chains. As shown in Figure 2.8, epoxy functional group is made up of two carbon atoms bonded chemically with one oxygen atom (Johanssen et al., 2011). This epoxy functional group can also be called as epoxide group or oxirane group (Hamerton, 1997; Kanerva, 2010; Minges, 1989). In general, epoxy functional groups show diverse chemical reactions towards various reagent types, such as amide, amine, anhydride, inorganic acid, alcohol, etc. The high reactivity of epoxy functional groups towards other functional groups is mainly due to the ring-strain phenomenon, as a result of the geometry of the oxirane groups (Tan, 2010). Also, cured epoxy resins possess unique properties, such as outstanding corrosion resistance, excellent chemical resistance, good mechanical properties, high adhesive strength and low shrinkage during cure (Koleske, 1995; Zaikov et al., 2005; Sheppard, 1986).

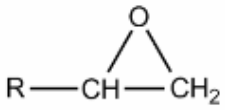

Figure 2.8: Three membered-ring structure of epoxy group (Petrie, 2000)

Diglycidyl ether of bisphenol-A (DGEBA) as illustrated in Figure 2.9 is one of the many types of epoxy resin commercially used nowadays. Commonly, DGEBA is produced via the dehydrohalogenation process of bisphenol-A and epichlorohydrin in the presence of sodium hydroxide (Riegel & Kent, 2003; Kanerva, 2010; Goosey, 1999). The uncured DGEBA resin can be crosslinked to form thermoset when treated with an appropriate curing agent. The DGEBA resin can be cured with or without the presence of thermal heat (Sheppard, 1986). However, the curing process of DGEBA resin is more time-consuming if compared to that of the other types of thermosetting resins (Wiley, 1988). Basically, the cured DGEBA thermoset maintain its three-dimensional network structure once being cured. In other words, the cured thermoset is unable to be re-softened under heat once they are cured (Kanerva, 2010).

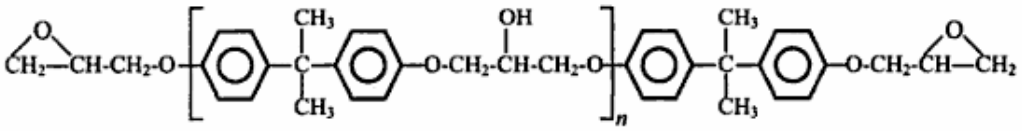

Figure 2.9: Diglycidyl ether of bisphenol A (DGEBA) structure
(Zaikov et al., 2005)

2.4.2 Vinyl Ester Resin

Vinyl ester resin as displayed in Figure 2.10 is an unsaturated thermosetting resin. Generally, vinyl ester resin is commercially prepared via the chemical reaction between the bisphenol-A and methacrylic acid, in the presence of styrene monomers (Campo, 2008; Maier & Calafut, 1998). The unsaturated carbon-carbon double bonds

in the uncured vinyl ester resins could be crosslinked when treated with the peroxides, such as the methyl ethyl ketone peroxide (MEKP). Black & Hastings (1998) and Hoa (2009) also found that the addition of MEKP into the vinyl ester resin can initiate the polymerization or crosslinking process of the uncured resin.

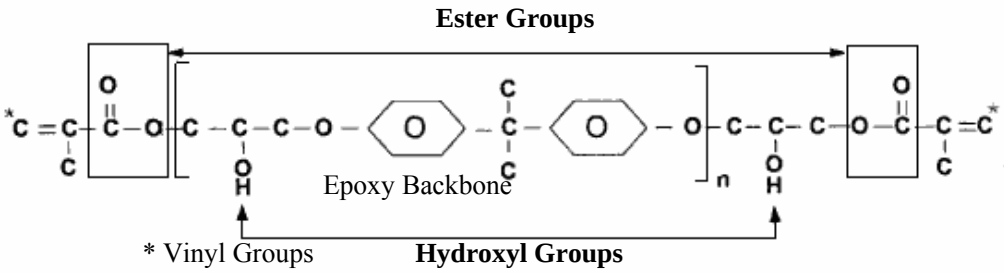

Figure 2.10: Vinyl ester resin structure (Kulshreshtha & Vasile, 2002)

In general, vinyl ester thermosets possess excellent chemical resistance, good creep and fatigue resistance, and relatively long durability (Fakirov & Bhattacharyya, 2007; Campo, 2008; Maier & Calafut, 1998; Scheirs, 2009). Vinyl ester is commonly used as matrices for composite materials, coating, and building materials. Also, vinyl ester resin is widely utilized in automotive and electronic industries (Maier & Calafut, 1998; Kulshreshtha & Vasile, 2002).

2.4.3 Unsaturated Polyester Resin

As illustrated in Figure 2.11, unsaturated polyester resin is made up of a short chain of the polyester with an unsaturated C=C double bond in its backbone chain, attached with a vinyl monomer (Scheirs & Long, 2003; Feldman & Barbalata, 1996; Fink, 2005). The polymerizable C=C double bond in unsaturated polyester resin can chemically react with the styrene monomer through the free radical polymerization to form the solid thermoset with infusible three-dimensional crosslink network structure. Also, methyl ethyl ketone peroxide (MEKP) can be utilized as a catalyst to promote